

U.S. DEPARTMENT OF COMMERCE PATENT AND TRADEMARK OFFICE		ATTORNEY'S DOCKET NUMBER KAPPE=1
TRANSMITTAL LETTER TO THE UNITED STATES DESIGNATED/ELECTED OFFICE (DO/EO/US) CONCERNING A FILING UNDER 35 U.S.C. 371		U.S. APPLICATION NO. (if known, see 37 CFR 1.5) C97369956
INTERNATIONAL APPLICATION NO. PCT/EP00/11069	INTERNATIONAL FILING DATE November 9, 2000	PRIORITY CLAIMED November 10, 1999
TITLE OF INVENTION ZINC SULPHIDE ELECTROLUMINOPHORES AND METHOD FOR PRODUCTION THEREOF		
APPLICANT(S) FOR DO/EO/US Frank KAPPE et al.		
<p>Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:</p> <ol style="list-style-type: none"> 1. <input checked="" type="checkbox"/> This is a FIRST submission of items concerning a filing under 35 U.S.C. 371. 2. <input type="checkbox"/> This is a SECOND or SUBSEQUENT submission of items concerning a filing under 35 U.S.C. 371. 3. <input checked="" type="checkbox"/> This is an express request to begin national examination procedures (35 U.S.C. 371(f)) at any time rather than delay examination until the expiration of the applicable time limit set in 35 U.S.C. 371(b) and PCT Articles 22 and 39(1). 4. <input type="checkbox"/> The US has been elected in a Demand by the expiration of 19 months from the priority date (PCT Article 31). 5. <input checked="" type="checkbox"/> A copy of the International Application as filed (35 U.S.C. 371(c)(2)) <ol style="list-style-type: none"> a. <input type="checkbox"/> is attached hereto (required only if not transmitted by the International Bureau). b. <input checked="" type="checkbox"/> has been communicated by the International Bureau. c. <input type="checkbox"/> is not required, as the application was filed in the United States Receiving Office (RO/US). 6. <input type="checkbox"/> An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)). 7. <input checked="" type="checkbox"/> Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371(c)(3)) <ol style="list-style-type: none"> a. <input type="checkbox"/> are transmitted herewith (required only if not transmitted by the International Bureau). b. <input type="checkbox"/> have been communicated by the International Bureau. c. <input type="checkbox"/> have not been made; however, the time limit for making such amendments has NOT expired. d. <input checked="" type="checkbox"/> have not been made and will not be made. 8. <input type="checkbox"/> An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)). 9. <input type="checkbox"/> An oath or declaration of the inventor(s) (35 U.S.C. 371(c)(4)). 10. <input type="checkbox"/> An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371(c)(5)). <p>Items 11. to 16. below concern document(s) or information included:</p> <ol style="list-style-type: none"> 11. <input type="checkbox"/> An Information Disclosure Statement under 37 CFR 1.97 and 1.98. 12. <input type="checkbox"/> An Assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included. 13. <input checked="" type="checkbox"/> A FIRST preliminary amendment. <input type="checkbox"/> A SECOND or SUBSEQUENT preliminary amendment. 14. <input type="checkbox"/> A substitute specification. 15. <input type="checkbox"/> A change of power of attorney and/or address letter. 16. <input checked="" type="checkbox"/> Other items or information: <ul style="list-style-type: none"> <input checked="" type="checkbox"/> Courtesy copy of the International Application as filed (In German). <input checked="" type="checkbox"/> Courtesy copy of the first page of the International Publication (WO 01/34723). <input checked="" type="checkbox"/> Formal drawings, 2 sheets, Figures 1-2. <input checked="" type="checkbox"/> Courtesy Copy of the International Search Report. <input checked="" type="checkbox"/> Application Data Sheet. <p><input checked="" type="checkbox"/> The application is (or will be) assigned to: Bundesdruckerei GmbH, whose address is Oranienstrasse 91, D-10958 Berlin, Germany and Leuchtstoffwerke Breitung GmbH whose address is Lange Sömmme 17, D-98597 Breitung, Germany</p>		

U.S. APPLICATION NO. (If known, see 37 CFR 1.5) <div style="font-size: 24pt; font-weight: bold;">09/869956</div>	International Application No PCT/EP00/11069	Attorney's Docket No KAPPE=1
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17. ☒ The following fees are submitted:

BASIC NATIONAL FEE (37 CFR 1.492 (a)(1) –(5):
 Neither international preliminary examination fee (37 CFR 1.482)
 nor international search fee (37 CFR 1.445(a)(2)) paid to USPTO
 and International Search Report not prepared by the EPO or JPO... ..\$1000.00

International preliminary examination fee (37 CFR 1.482) not paid to
 USPTO but International Search Report prepared by the EPO or JPO... ..\$860.00

International preliminary examination fee (37 CFR 1.482) not paid to USPTO but
 international search fee (37 CFR 1.445(a)(2)) paid to USPTO.....\$710.00

International preliminary examination fee paid to USPTO (37 CFR 1.482)
 but all claims did not satisfy provisions of PCT Article 33(1)-(4).... ..\$690.00

International preliminary examination fee paid to USPTO (37 CFR 1.482)
 and all claims satisfied provisions of PCT Article 33(1)-(4).....\$100.00

ENTER APPROPRIATE BASIC FEE AMOUNT =

Surcharge of **\$130.00** for furnishing the oath or declaration later than [X] 20 [] 30
 months from the earliest claimed priority date (37 CFR 1.492(e)).

Claims as Originally Presented	Number Filed	Number Extra	Rate		
Total Claims	- 20		X \$18.00	\$	
Independent Claims	- 3		X \$80.00	\$	
Multiple Dependent Claims (if applicable)			+\$270.00	\$	

TOTAL OF ABOVE CALCULATIONS =

Claims After Post Filing Prel. Amend	Number Filed	Number Extra	Rate		
Total Claims	- 20		X \$18.00	\$	
Independent Claims	- 3		X \$78.00	\$	

TOTAL OF ABOVE CALCULATIONS =

Reduction of ½ for filing by small entity, if applicable Applicant claims small entity
 status. See 37 CFR 1.27

SUBTOTAL =

Processing fee of **\$130.00** for furnishing the English translation later than [] 20 [] 30
 months from the earliest claimed priority date (37 CFR 1.492(f)).

TOTAL NATIONAL FEE =

Fee for recording the enclosed assignment (37 CFR 1.21(h)). The assignment must be
 accompanied by an appropriate cover sheet (37 CFR 3.28, 3.31). **\$40.00** per property +

TOTAL FEES ENCLOSED =

Amount to be:	\$
refunded	
charged	\$

CALCULATIONS PTO USE ONLY

a. ☐ A check in the amount of \$_____ to cover the above fees is enclosed.

b. ☒ Credit Card Payment Form (PTO-2038), authorizing payment in the amount of \$1,120.00, is attached.

c. ☐ Please charge my Deposit Account No. **02-4035** in the amount of \$_____ to cover the above fees.
 A duplicate copy of this sheet is enclosed.

d. ☒ The Commissioner is hereby authorized to charge any additional fees which may be required, or credit any overpayment
 to Deposit Account No. **02-4035**. A duplicate copy of this sheet is enclosed.

NOTE: Where an appropriate time limit under 37 CFR 1.494 or 1.495 has not been met, a petition to revive (37 CFR 1.137(a) or
 (b)) must be filed and granted to restore the application to pending status.

SEND ALL CORRESPONDENCE TO:

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 Date of this submission: **July 10, 2001**

SIGNATURE
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 NAME
 25.618.
 REGISTRATION NUMBER

PTO/PST Rec'd 18 OCT 2001

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:) Art Unit:
)
Frank KAPPE et al)
)
IA No.: 09/869,956)
) Washington, D.C.
IA Filed: November 9, 2000)
)
U.S. App. No.:)
(Not Yet Assigned))
) October 15, 2001
National Filing Date:)
(Not Yet Received))
)
For: ZINC SULFIDE ELECTROLUMINOPHORES Docket No.: KAPPE-1

PRELIMINARY AMENDMENT

Honorable Commissioner for Patents and Trademarks
Washington, D.C. 20231

Sir:

Prior to examination upon the merits, kindly amend
as follows:

IN THE CLAIMS

Please cancel use claims 30 and 31.

REMARKS

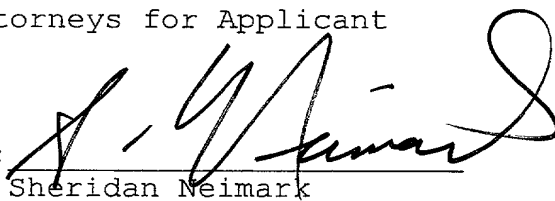
The above amendments to the claims are being made in
order to eliminate the non-statutory use claims and for the
purpose of reducing the filing fee. Please enter this
amendment prior to calculation of the filing fee in this case.

In re of: KAPPE-1

Favorable consideration and allowance are earnestly solicited.

Respectfully submitted,
BROWDY AND NEIMARK, P.L.L.C.
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By:



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F:\,R\rieb\Kappel\PTO\Preliminary Amendment.doc

FILED OCT 1 1998

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:) Art Unit:
Frank KAPPE et al.)
)
IA No.: PCT/EP00/11069)
) Washington, D.C.
IA Filed: November 9, 2000)
)
U.S. App. No.:)
(Not Yet Assigned))
) July 10, 2001
National Filing Date:)
(Not Yet Received))
)
For: ZINC SULPHIDE...) Docket No.: KAPPE=1

PRELIMINARY AMENDMENT

Honorable Commissioner for Patents and Trademarks
Washington, D.C. 20231

Sir:

Contemporaneous with the filing of this case and
prior to calculation of the filing fee, kindly amend as
follows:

IN THE SPECIFICATION

After the title please insert the following
paragraph:

REFERENCE TO RELATED APPLICATIONS

--The present application is the national stage
under 35 U.S.C. §371 of international application
PCT/EP00/11069, filed November 9, 2000 which designated the
United States, and which application was not published in the
English language.--

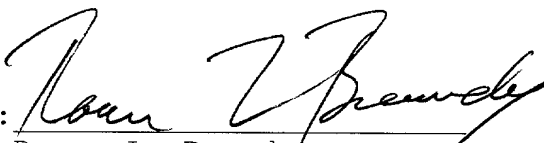
In re of: Frank KAPPE et al. (KAPPE=1)

REMARKS

The above amendment to the specification is being made to insert reference to the PCT application of which the present case is a U.S. national stage

Favorable consideration is earnestly solicited.

Respectfully submitted,
BROWDY AND NEIMARK, P.L.L.C.
Attorneys for Applicant

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PCT " 9909090

Zinc Sulfide Electroluminophores and Methods for Their Production

The present invention relates to zinc sulfide (ZnS) based fine-grain electroluminescent phosphors and methods for their production.

Phosphors of this type are generally doped with copper (Cu), however, optionally also with copper and/or gold (Au), as well as with copper and manganese (Mn) and they furthermore contain one or more coactivators, for which purpose halide anions (Cl, Br, I) or certain tervalent cations (e.g., Al, Ga, In) are usually inserted into the ZnS lattice.

In dependence upon their specific chemical composition, the zinc sulfide electroluminophores emit in the blue, green or yellow-orange range of the visible spectrum. In technical applications they are used to manufacture electroluminescent lamps that are used either for the background lighting of LCD displays (clocks, pocket calculators, mobile telephones, instrument lighting, etc.) or as luminous and marking elements, e.g., in airplanes and motor vehicles, in the interior and on the facades of buildings, as well as in advertising fixtures, etc.

It is known that zinc sulfide electroluminophores, as compared to technical luminescent substances for the UV, X-ray and cathode ray excitation, have a comparatively short life. The half-life (which is the time in which the brightness of the EL phosphors decreases to half its original value) of unencapsulated electroluminophores is only a few hundred hours. It is widely believed that their service life is significantly influenced, among other factors, by the grain size of the electroluminophores. This is one of the reasons why commercially available ZnS EL phosphors typically have average grain sizes in the range of 20 to 40 μm .

However, the extent to which pigments of such a large size can be made into high-quality layers is

limited. In the commonly used screen printing techniques, for example, they require the use of comparatively large screens, resulting in dry layer thicknesses of up to 40 μm . These often display a visibly uneven EL emission due to the unavoidable inhomogeneities of such layers.

Another shortcoming of the resulting thick electroluminescent arrangements that is attributable to the large grain size of commercially available EL pigments lies in the fact that relatively high supply voltages are required to attain the desired levels of brightness. These can result in high stresses on the incorporated binding agents and thus in a reduction in the service life of the EL arrangements.

Moreover, with the use of the coarse EL pigments according to the prior art, it is possible that individual particularly large luminophore particles can protrude from the layer despite the adjusted layer thickness of up to 40 μm . In these cases the voltage stability and/or electric strength of the EL films is reduced, resulting in an additional reduction in their service life.

A significant reduction in the average grain size of the EL phosphors and simultaneous preservation or improvement of the brightness and durability values is therefore highly desirable for many technical applications that are based on the use of screen printing processes.

If, as recently proposed in DE 19 708 543, EL pigments are even to be processed into fine graphic structures, such as security elements in the field of value product printing by means of intaglio or offset printing processes, the availability of fine-grain EL phosphors must be considered an essential prerequisite for the technical feasibility of such an application. Experience has shown that it is necessary in this case to use average pigment grain sizes of 2 to

6 μm to be able to meet the technical requirements of these printing processes.

Methods for producing efficient EL phosphors have been known for a long time. The pertinent prior art is described, for example, in U.S. Patent No. 4,859,361 and in WO 91/16722.

According to those patent documents, the following steps are required to produce Cu doped or Cu and Mn doped ZnS electroluminophores that are coded with the usual coactivators:

Step 1: Preparation of a mixture of ZnS, the desired quantity of an EL activator (e.g., CuSO_4) and a coactivating, halide-containing fluxing agent (usually BaCl_2 , MgCl_2 , NaCl).

Step 2: Firing of this mixture at temperatures between 1000 and 1300°C.

Step 3: Cooling of the fired material to room temperature and rinsing with water.

Step 4: Mechanical working of the material by milling.

Step 5: Renewed firing of the thusly treated material in the temperature range between 600 and 900°C, optionally after previous renewed addition of ZnSO_4 and CuSO_4 .

Step 6: Cooling to room temperature and optional quenching with H_2O after a certain cooling time.

Step 7: Optional washing with H_2O and/or mineral acids to remove soluble components and with KCN solution to remove excess Cu_2S .

Particular importance is attached by the invention to the 4th preparation step. The mechanical working of the material that was first fired at 1000 to 1300°C is intended to transform a portion of the hexagonal ZnS electroluminophore formed under these conditions into the cubical crystal

form. It is alleged that a transformation of this type effects an improvement of the brightness of the EL phosphors and particularly increases their life.

When the described process and comparable process variations are used, zinc sulfide electroluminophores with average grain sizes between 20 and 40 μm are obtained and individual particles may still significantly exceed this range of grain sizes. This can be attributed mostly to the high firing temperatures, as well as to the use of fluxing agents with a strongly mineralizing effect. Electroluminophores of this grain size class have the above-described shortcomings.

In patent document US 5,643,496, the process is modified to the extent that zinc sulfide electroluminophores can be obtained that have a grain size smaller than 23 μm , preferably 21 μm , and which, by adjusting the temperature of the first firing process to between 1100 and 1190°C, preferably to 1160°C, allegedly reach the level of 25 μm large ZnS electroluminescent materials regarding their attainable levels of brightness and half lives.

Such a minor reduction in the average grain size of the electroluminophores hardly results in any noticeable improvements even for the use in screen printing processes. The principal shortcomings of EL phosphor particles of this coarseness largely still exist.

Average EL pigment grain sizes in the range of 10 μm can allegedly be attained with a process according to US 5,635,111; however, the solution described in that patent document has significant technical shortcomings. These lie in the fact that, on one hand, the firing is performed in a complicated vacuum apparatus in the presence of extremely aggressive and toxic gases (halogen halides, H_2S), which involves the associated risks if the apparatus should fail. On the other hand, the very time consuming and expensive process hardly appears suitable for producing

larger quantities of EL luminophores under technical conditions. The present invention is therefore based on the object of creating a novel, cost-effective method for producing fine-grain zinc sulfide electroluminophores that can be made into efficient and long-lived electroluminescent layers of a high quality with various printing techniques.

In accordance with the present invention this object is met with the technical teaching of claim 1.

The inventive process is characterized accordingly by the following preparation steps and measures:

Step 1: Preparation of special, fine-grain zinc sulfides and use of these materials as a starting product for the synthesis of the inventive fine-grain zinc sulfide electroluminophores.

The preparation of zinc sulfide starting materials of this type takes place by precipitation of ZnS from the solutions of zinc salts, such as e.g., ZnSO_3 , $\text{Zn}(\text{NO}_3)_2$ and ZnCl_3 , preferably from zinc sulfate solutions, with the aid of induced H_2S gas or resulting from the addition of H_2S -generating compounds at temperatures of 20 to 80°C and a pH between 0.5 and 3.0. The zinc ion concentration of the given zinc salt solutions is adjusted to values of 0.25 moles/l to 2.0 moles/l.

This precipitation reaction produces as a result fine-grain zinc sulfides with very narrow grain-size distributions and the desired average grain size can be controlled by guiding the process parameters, such as, e.g., the zinc ion concentration, the speed with which the H_2S is passed in, the stirring speed, the temperature, and the pH.

The average grain sizes of the zinc sulfides prepared according to this invention and used as the starting material for the synthesis of the inventive electroluminophores are typically 2 to 20 μm ,

preferably 2 to 5 μm or 5 to 15 μm .

This is a significant advantage compared to the prior art, because fine-grain zinc sulfides are already generated in this process step by purely preparative means, i.e., without the use of time-consuming sifting or harmful milling processes, and their grain size distribution is then transferred to the inventive electroluminophores by the specific design of the subsequent process steps and largely maintained throughout the sequential performance of these steps.

A further advantage lies in the fact that, in addition to the grain sizes, the surface properties of the ZnS precipitation products can also be controlled via the specific selected precipitation conditions.

This results in compact ZnS crystallites with a very low tendency to form agglomerates. These special morphological characteristics of the ZnS starting materials prepared according to this invention advantageously affect the grain structure and the performance of the resulting inventive electroluminophores.

Step 2: Mixing of the fine-grain ZnS starting materials produced according to this invention with the activator-coactivator compounds required for the luminophore formation.

The copper and/or gold compounds, or copper and/or gold and manganese compounds (e.g., CuSO_4 , $\text{HAuCl}_4 \cdot 4 \text{H}_2\text{O}$, MnSO_4) as well as aluminum compounds (e.g. $\text{Al}(\text{NO}_3)_3$) that may be required for the coactivation may already be added during the precipitation of the ZnS or also to the washed ZnS suspension after completion of the precipitation. This permits a homogeneous distribution of the activators and coactivators in the preparation mixture that is advantageous for the process of the luminophore formation, and also a close contact between the activator, coactivator and ZnS particles.

However, it is also possible to dry mix the activator and coactivator compounds and the zinc sulfide prepared according to this invention. In this case a preferred process variant consists of first homogenizing the activator and coactivator compounds with a portion of the dried ZnS and then blending this mixture with the remaining amount of ZnS that is required to ensure the desired luminophore composition.

To this mixture the fluxing agents, which are described in more detail below, are then added as well:

Step 3: A one to ten-hour firing of the mixture at temperatures below 1000°C, preferably in the temperature range between 800 and 1000°C in air or in an inert nitrogen atmosphere or in an atmosphere consisting of a mixture of nitrogen and 1 to 10% hydrogen in the presence of fluxing agents with an only slightly mineralizing action selected from the compound classes of the fluorides, bromides and iodides.

After completion of the firing process, the fired product is then cooled to room temperature, subsequently washed with deionized water and then optionally filtered and dried.

In this manner it is effectively ensured that the average grain size and grain size distribution of the zinc sulfide electroluminophores after completion of the firing process and processing of the fired product essentially conform to the ZnS starting material prepared according to this invention and used for the luminophore synthesis. The inventive fine-grain ZnS electroluminophores that are obtained with this process step have typical medium grain sizes between 2 and 20 µm, preferably between 2 and 5 µm or 5 and 15 µm.

It is important compared to the prior art that the described firing process is performed at temperatures below 1000°C and that the presence, especially of chloride-containing or strongly mineralizing fluxing agents is completely abstained from. While it is true that the use of fluoride and/or bromide and/or iodide-containing fluxing agents does enhance the reconstruction of the ZnS lattice and the targeted inclusion of the activators required for the formation of the luminophores, their operating mechanisms are such that the grain growth can effectively be limited in the described temperature range.

The fluxing agents that are used according to this invention can, at the same time, function as a source for the insertion of the coactivators. For this purpose they optionally receive certain tervalent cationic components (e.g. Al^{3+} , Bi^{3+}) in addition to the above halide anions.

A further advantage of the inventive process compared to the prior art lies in the fact that the synthesized electroluminophores remain completely in their cubic crystal modification because of the firing temperature being limited to a maximum of 1000°C. As will be described later, this fact results in advantages regarding the attainable levels of brightness and half-life of the inventive electroluminophores. In processes representing the prior art, hexagonally crystallizing ZnS electroluminophores are obtained initially. These are subsequently subjected to an intense and often harmful mechanical milling process in order to achieve an at least partial reverse transformation to the cubic structure type. The related shortcomings are prevented in advance with the present inventive process.

Step 4: Treatment of the powdery electroluminophores obtained after the main firing process with organic and inorganic acids.

The fine-grain zinc sulfide phosphors obtained after the implementation of preparation steps 1 through 4 are characterized by high photo and cathode luminescence yields. This fact is an indication of the effective inclusion of the activators and coactivators into the ZnS lattice as well as of the high effectiveness of the luminescence processes that occur under these excitation conditions.

It needs to be noted, however, that the phosphors that have been synthesized in this manner do not yet have optimum electroluminescent properties.

The efficiency of the electroluminescence can be increased significantly, however, if the zinc sulfide luminophore powder is subjected to a treatment with organic or inorganic acids, such as hydrochloric acid (HCl), sulfuric acid (H₂SO₄), acetic acid, or citric acid after the main firing process.

For this purpose the zinc sulfide phosphors obtained according to this invention are suspended in certain quantities of the solutions of these acids at temperatures between 20 and 60°C, preferably at room temperature, while stirring and the retention time of the luminophore particles in the given acid bath may span a range from 10 minutes up to 10 hours depending upon the type and concentration of the chosen acid, as well as on the chosen temperature. The powdery ZnS electroluminophores are subsequently filtered out, washed to pH neutrality and optionally dried at temperatures of 100 to 120°C.

As shown by electron-microscopic examinations, the inventive finest-grain electroluminophores show a clearly changed morphology of the crystallites after this acid treatment. It is characterized by a high roughness of the crystallite surfaces as well as by the formation of grooves, corners,

edges and other structural defects. Such a modification of the habit of the doped ZnS crystallites apparently is an important prerequisite for the increase in the electroluminescence yields of the zinc sulfide luminophores that is noted after the acid treatment.

An advantageous secondary effect of the described acid treatment lies in the further reduction of the average grain size of the luminophore particles, as well as in the further narrowing of the grain size distributions. The scope of this effect can be controlled via the conditions of the acid treatment. The acid treatment furthermore enhances the de-agglomeration of the luminophore particles, resulting in additional advantages for the use of the inventive luminophores in electroluminescent layers (dispersion behavior, layer homogeneity).

Step 5: Re-doping of the finest-grain electroluminophores that have been synthesized according to this invention with certain quantities of activator and/or coactivator ions.

Even with the inventive process it is possible to further increase the EL efficiency through the customary repeated addition of certain quantities of activator compounds, particularly of CuSO_4 and/or coactivator compounds, particularly those containing Al^{3+} ions, and renewed firing of the resulting solids mixtures at temperatures between 300 and 800°C. In this manner a fine adjustment of the activator and/or coactivator concentrations and distribution of the active luminescence centers is achieved in the ZnS matrix.

After a firing time of preferably 30 minutes to 10 hours, the fired product is cooled to room temperature and subsequently washed with H_2O , mineral acids (e.g., HNO_3), or KCN solution to remove activator and/or coactivator compounds that were not inserted into the ZnS lattice and have precipitated on the surface.

For screen printing applications, inventive zinc sulfide electroluminophores with average grain sizes of 5 to 20 μm are used. Electroluminophores with these dimensions can be advantageously processed into high-performance EL lamps with a significantly improved layer structure.

Inventive fine-grain electroluminophores with average grain sizes between 2 and 5 μm , on the other hand, are particularly suitable for applications in intaglio or offset printing. They permit the implementation of fine electroluminescent graphic structures, e.g., as security marks in value product printing.

In any case, the inventive luminophores are characterized by a brightness-service life relationship that is adapted to the given application and optimal with respect to the adjusted grain size.

Moreover, studies have confirmed that EL elements can be constructed using electroluminophores with average grain sizes of 6 μm produced according to this invention that display levels of brightness and half lives which, under identical operating conditions, are comparable to EL films manufactured from commercially available coarse-grained EL pigments with grain sizes of 20 to 40 μm .

As previously mentioned, the surprisingly high service life of the electroluminophores produced according to this invention, especially of those EL pigments that have average grain sizes of 2 to 5 μm in accordance with this invention, is very likely attributable to their cubic crystal structure, which deviates from the commercially available EL pigments.

According to the prior art this is considered advantageous for attaining high levels of brightness and stability.

To further improve the stability, the individual crystallites of the inventive electroluminophores may also be provided with suitable protective layers according to the prior art. Numerous methods and materials are known for applying such protective layers.

Further details and advantages of the invention will be explained below based on examples and drawings.

Example 1

10 l of a 1.4 molar ZnSO_4 solution are entered into a reaction vessel. The pH of this solution is subsequently adjusted to 1.0 under addition of sulfuric acid (H_2SO_4).

The precipitation of the fine-grain zinc sulfide takes place by passing H_2S gas into the prepared solution while stirring (stirring speed 700 rpm). The volume flow of the H_2S gas is 36 l/h, the work is performed at a reaction temperature of 60°C.

After a reaction time of approximately 500 min. the H_2S flow is stopped. Any H_2S still remaining in the reaction vessel is exhausted, the obtained ZnS suspension is decanted, repeatedly washed with deionized water and finally filtered off. The obtained fine-grain ZnS powder is subsequently dried at a temperature of 120°C.

Curve 1 in Figure 1 shows the grain size distribution of the fine-grain zinc sulfide prepared in this manner, which was determined with the aid of a Coulter counter grain size measuring instrument.

What is striking is the very narrow distribution of the ZnS grain sizes (the so-called QD value, which is calculated based on the equation $\text{QD} = (d_{75} - d_{25}) / (d_{75} + d_{25})$, may be regarded as a measure for the range of the distribution, which, in the present case is $\text{QD} = 0.134$); a d_{50} value of

4.7 μm was determined for the average grain size of the ZnS material prepared according to the above described process.

In the next step a certain amount of the obtained zinc sulfide is stirred into a copper sulfate solution. After concentrating and drying of this suspension at approximately 120°C , the material, which is now present as a mixture of solids, is once again homogenized dry and subsequently sifted with a 35 μm gauze. The weighed-in quantities of ZnS and CuSO_4 are calculated such as to establish a copper content of 1.5% for the zinc sulfide copper “activator”.

A comparable process is also used in the preparation of a corresponding BiI_3 “activator”. In the example described here, the BiI_3 content of the ZnS- BiI_3 mixture is 8.5%.

The preparation of the batch subsequently takes place by a thorough blending of 1.65 kg of the fine-grain zinc sulfide, 81.5 g of the copper “activator”, 7.5 g of the ZnS- BiI_3 mixture, as well as 5.2 g aluminum fluoride (AlF_3). This mixture is entered into covered quartz pans and fired for 2 hours at a temperature of 980°C in an N_2/H_2 atmosphere with a hydrogen content of 1.5%

After completion of the firing process, the fired material is cooled to room temperature and repeatedly washed with deionized water.

This is followed by the acid treatment of the obtained material. For this purpose the washed fired material is entered into an acid bath and 2 l H_2O and 500 ml of a 37% hydrochloric acid are added relative to 1 kg of the fired material while stirring. After a retention time of one hour, this is followed by decanting and washing with deionized water to pH neutrality.

The renewed addition of copper sulfate to this aqueous suspension serves to re-dope the

luminophore material. The amount of CuSO_4 used for this purpose is calculated according to the ratio of 2 g Cu per 1 kg luminophore.

After concentration by evaporation and drying of the suspension, the dry material is fired in open quartz pans for 2 hours at 600°C in air. This is followed by an acid wash with 10% HNO_3 as well as repeated washing with H_2O to pH neutrality. This is followed by decanting, filtering and drying.

In a concluding process step, the obtained material is once again annealed in open quartz pans for 2 hours at 300°C in air and homogenized by sifting after it has cooled off.

As a result of these preparation steps a ZnS-CU luminophore with a green electroluminescence is obtained that is characterized by a high level of brightness and long half-life. The average grain size of the powdery electroluminophore is $5.2\ \mu\text{m}$ ($\text{QD} = 0.265$). As can be seen from Fig. 1 (Curve 2), the average grain size of the EL pigment prepared according to the example is only significantly above that of the ZnS starting material used in this process.

Example 2

As in example 1, the precipitation of the zinc sulfide takes place after H_2S gas is passed into a ZnSO_4 solution, however, the reaction parameters are adjusted differently. The reaction is started with a 0.25 molar ZnSO_4 solution, the pH is fixed to 1.6, the H_2S volume flow is 60 l/h and the reaction temperature is 40°C .

The zinc sulfide that is present in the suspension after completion of the precipitation reaction has an average grain size of $17.0\ \mu\text{m}$ ($\text{QD} = 0.174$, see Fig. 2, curve 1). The obtained ZnS suspension

is washed repeatedly with deionized water and decanted; afterwards a sufficient amount of copper sulfate is added to establish a copper concentration of the ZnS material of 200 ppm after the activation. The copper activated ZnS suspension is transferred to drying pans and dried at 120°C.

To prepare the starting mixture for the firing process, 1.75 kg of the activated zinc sulfide, 0.5 g BiI_3 and 2.5 AlF_3 are thoroughly blended. The firing takes place in covered quartz firing pans at 990°C in air. The firing time is 5 hours.

After cooling the fired product to room temperature and washing it with deionized water, a 5-hour acid treatment is performed with 20% citric acid. This is followed by decanting and washing with H_2O to pH neutrality.

The re-doping of the luminophore material again takes place through addition of copper sulfate (502.5 mg per 1 kg luminophore) to the aqueous ZnS:Cu suspension.

After concentration by evaporation and drying of the suspension the dry product is fired in open quartz pans for 3 hours at 700°C in air. This is followed by treatment with 10% HNO_3 and repeated washing with H_2O (to pH neutrality), decanting, filtering and drying.

The concluding annealing of the zinc sulfide electroluminophore takes place in open quartz pans for 1 hour at 500°C in air, followed by cooling and sifting.

The resulting ZnS:Cu luminophore has an intense blue electroluminescence, as well as a long half-life. As shown by Curve 2 in Fig. 2, the d_{50} value of the grain size distribution of the inventive electroluminophore presented in this example, which describes the average grain size, is 14.5 μm ($\text{QD} = 0.156$) and thus somewhat below the value determined for the corresponding ZnS starting

material.

What is claimed is:

1. A method for producing zinc sulfide electroluminophores using the following process steps:
 1. Preparation of a fine-grain zinc sulfide by precipitation of zinc sulfide from the solutions of suitable zinc salts with H_2S .
 2. Mixing of the obtained fine-grain zinc sulfide with the activator and coactivator compounds required for the luminophore synthesis.
 3. Firing of the obtained mixtures in the temperature range of 800 up to a maximum of $1000^{\circ}C$ in the presence of fluxing agents with an only slightly mineralizing effect selected from the compound classes of the fluorides and/or bromides and/or iodides.
 4. Treatment of the powdery electroluminophores obtained according to step 3 with organic and/or inorganic acids in an acid bath while stirring, as well as washing, neutralizing and optionally filtering off and drying the zinc sulfide electroluminophores.
2. A method according to claim 1, characterized in that the precipitation of the fine-grain zinc sulfide takes place by passing H_2S into zinc salt solutions, such as $ZnSO_4$, $Zn(NO_3)_2$ and $ZnCl_2$, preferably by passing H_2S into zinc sulfate solutions with zinc ion concentrations of 0.25 moles/l to 2.0 moles/l at temperatures between 20 and $80^{\circ}C$ and a pH of 0.5 to 3.0.
3. A method according to claim 1 and 2, characterized in that the activator and coactivator compounds required in process step 2 are added to the washed ZnS suspension as early as during the precipitation of the fine-grain zinc sulfide taking place during the first process step, or immediately after completion of the precipitation.

4. A method according to claim 1, characterized in that the required activator and coactivator compounds are blended in process step 2 in dry form, initially with a portion of the washed and dried fine-grain zinc sulfide obtained after the first process step, and that this mixture is then combined with the remaining amount of fine-grain ZnS required to preserve the desired luminophore composition.
5. A method according to claim 3 and 4, characterized in that the added activator and coactivator compounds are copper sulfate and/or tetrachloroauric acid or the corresponding sodium salt and/or manganese sulfate and/or aluminum nitrate.
6. A method according to claim 1, characterized in that no strongly mineralizing fluxing agent, particularly no chloride-containing fluxing agent is added to the starting mixture for the firing process according to process step 3.
7. A method according to claim 1, characterized in that an only slightly mineralizing fluxing agent selected from the compound classes of the fluorides and/or bromides, and/or iodides is added to the starting mixture for the firing process according to process step 3, which contains, in addition to the halide anions, cationic components, e.g., Al^{3+} ions, that act as coactivators.
8. A method according to claim 6 and 7, characterized in that the firing in step 3 takes place in air or in an inert nitrogen atmosphere or in an atmosphere consisting of a gas mixture of nitrogen and 1 to 10% hydrogen.
9. A method according to claim 8, characterized in that the obtained fired material is cooled to

room temperature after completion of the firing process in step 3, washed with deionized water and subsequently optionally filtered and dried.

10. A method according to claim 1, characterized in that the acid treatment in process step 4 takes place in an acid bath with organic acids, e.g., acetic acid or citric acid, or with inorganic mineral acids, such as hydrochloric acid, nitric acid or sulfuric acid, with retention times of 10 minutes to 10 hours at temperatures between 20 and 60°C.
11. A method according to claim 10, characterized in that the acid treatment in process step 4 takes place with an approximately 37% HCl solution for 2 to 6 hours while stirring at room temperature.
12. A method according to claim 10, characterized in that the acid treatment in step 4 takes place with a 10 to 20% citric acid solution for 4 to 8 hours at 60°C while stirring.
13. A method according to any of claims 1 - 12, characterized in that after the washing, neutralizing and optionally performed filtering and drying of the electroluminophores obtained after step 4, a re-doping takes place in process step 5 with certain quantities of the activator and coactivator compounds.
14. A method according to claim 13, characterized in that the re-doping takes place with copper and/or gold and/or manganese and/or aluminum compounds.
15. A method according to claim 13 and 14, characterized in that the compounds used for the re-doping are preferably copper sulfate, and/or tetrachloroauric acid or the corresponding sodium salt and/or manganese sulfate and/or aluminum nitrate.

16. A method according to any of claims 13 - 15, characterized in that the re-doping takes place by means of a 30-minute to 10-hour firing in a temperature range between 300°C and 800°C.
17. A method according to any of claims 13 - 16, characterized in that the re-doping takes place in air or in an inert nitrogen atmosphere consisting of a mixture of nitrogen and 1 to 10% hydrogen.
18. A method according to any of claims 13 - 17, characterized in that, after cooling to room temperature, the firing product is washed with mineral acids, e.g., nitric acid and/or KCN solution to remove activator and/or coactivator materials that may have precipitated on the surface of the zinc sulfide electroluminophores.
19. A method according to any of claims 13 - 18, characterized in that the zinc sulfide electroluminophores are washed to pH neutrality with deionized water and subsequently filtered and dried after their treatment with mineral acids or KCN solution following the re-doping.
20. A method according to any of claims 1 - 19, characterized in that an annealing of the electroluminophores takes place in a 6th process step at a temperature in the range between 200° and 500°C, with the annealing time amounting from 30 minutes to 5 hours.
21. A method according to claim 20, characterized in that the annealing process takes place in air or in an inert nitrogen atmosphere or in an atmosphere consisting of a mixture of nitrogen and 1 to 10% hydrogen.
22. A zinc sulfide electroluminophore having a cubic crystal structure and characteristic

structural composition, characterized in that the luminophore particles have typical average grain sizes of 2 to 5 μm .

23. A zinc sulfide electroluminophore having a cubic crystal structure and characteristic structural composition, characterized in that the luminophore particles have typical average grain sizes of 5 to 15 μm .
24. A zinc sulfide electroluminophore according to claim 22 or 23, characterized in that the luminophore particles are coated with thin organic and/or crystalline or amorphous inorganic protective layers to further increase their service life.
25. A zinc sulfide electroluminophore according to claim 24, characterized in that the protective layer consists of an inner metal oxide film and an outer silicon nitrate film.
26. A zinc sulfide electroluminophore according to one or more of claims 22 - 25, characterized in that the luminophore particles are dispersible in a screen printing ink and preferably usable for printing in narrow-mesh screens (120 meshes/inch).
27. A zinc sulfide electroluminophore according to one or more of claims 22 - 25, characterized in that the luminophore particles are dispersible and usable for printing in a halftone photogravure ink or flexographic printing ink or offset printing ink or letterset printing ink or gravure printing ink.
28. A zinc sulfide electroluminophore according to one or more of claims 22 - 25, characterized in that the luminophore particles are applied onto thermal transfer films and transferable to printable material by means of transfer printing.

29. A zinc sulfide electroluminophore according to one or more of claims 22 - 25, characterized in that the luminophore particles are embedded in thermoplastic granule matrixes and processed into films by means of extrusion/coextrusion and/or thinfilm-casting.
30. Use of a zinc sulfide electroluminophore having an average grain size of 5 to 20 μm for screen printing.
31. Use of a zinc sulfide electroluminophore having an average grain size of 2 to 5 μm for application in intaglio or offset printing.

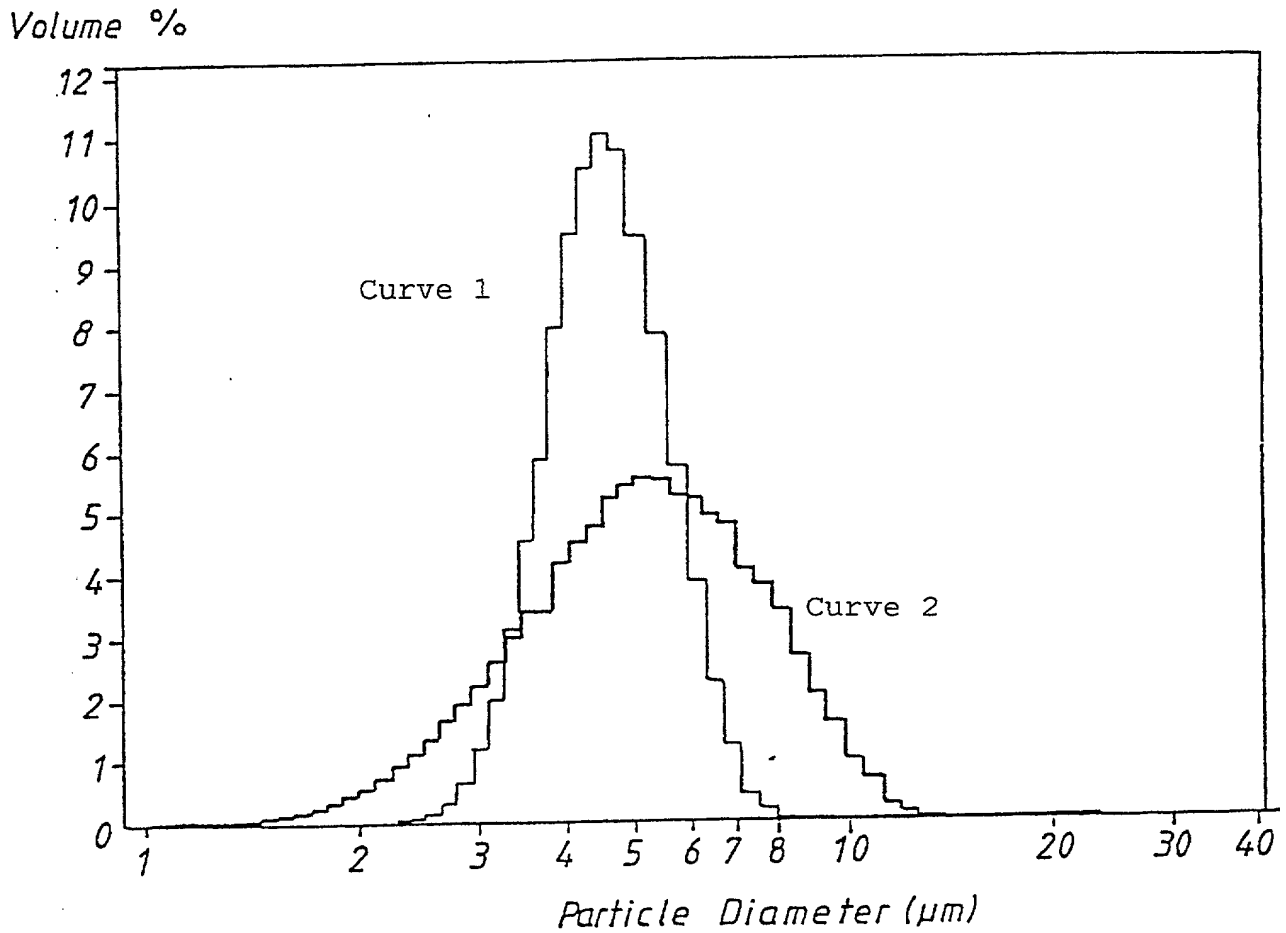


Figure 1

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Volume %

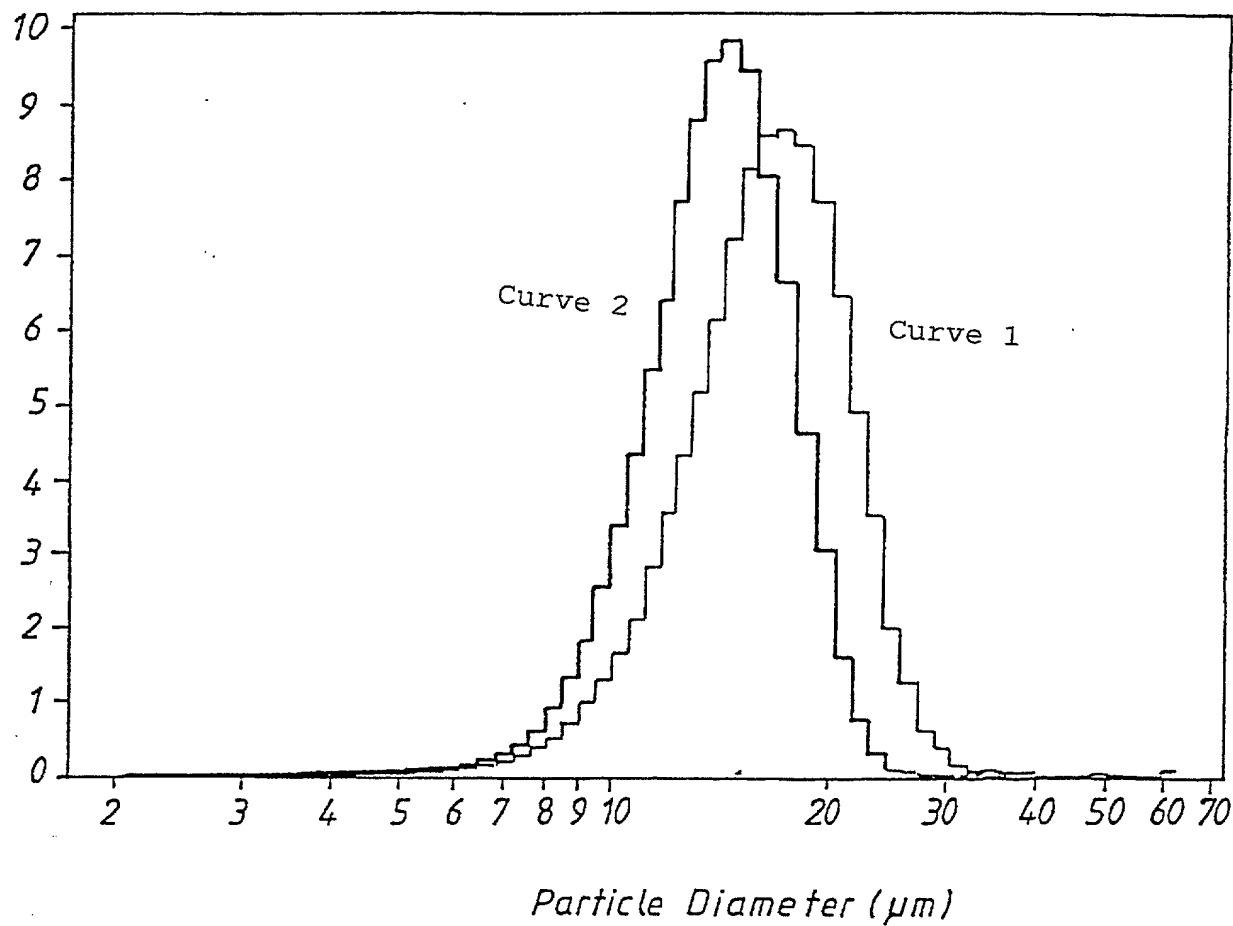


Figure 2

Combined Declaration for Patent Application and Power of Attorney

As a below-named inventor, I hereby declare that:

My residence, post office address and citizenship are as stated below next to my name; and that I believe I am the original, first and sole inventor (if only one name is listed below) or an original, first and joint inventor (if plural names are listed below) of the subject matter which is claimed and for which a patent is sought on the invention entitled

ZINC SULFIDE ELECTROLUMINOPHORES AND METHOD FOR PRODUCTION THEREOF

the specification of which (check one)

- [] is attached hereto;
 [] was filed in the United States under 35 U.S.C. §111 on _____, as
 U.S. Appln. No. _____*; or
 [x] was/will be filed in the U.S. under 35 U.S.C. §371 by entry into the U.S. national stage of an international
 (PCT) application, PCT/EP00/11069; filed 9 November 2000, entry requested on 10
July 2001*; national stage application received U.S. Appln. No. _____*;
 §371/§102(e) date _____* (* if known)

and was amended on _____ (if applicable).

(include dates of amendments under PCT Art. 19 and 34 if PCT)

I have reviewed and understand the contents of the above-identified specification, including the claims, as amended by any amendment referred to above; and I acknowledge the duty to disclose to the Patent and Trademark Office (PTO) all information known by me to be material to patentability as defined in 37 C.F.R. §1.56.

I hereby claim foreign priority benefits under 35 U.S.C. §§ 119 (a)-(d) and 365 (b) of any prior foreign application(s) for patent, inventor's or plant breeder's rights certificate(s), or under §365(a) of any PCT application which designated at least one country other than the U.S., listed below:

Application No.	Country	Filing Date (MM/DD/YYYY)
199 53 924.3	Germany	11/10/1999

If I claimed foreign priority above, I hereby identify below any foreign application for patent (including an international (PCT) application designating a country other than the United States) or for an inventor's or plant breeder's certificate, having a filing date before that of the earliest application from which foreign priority is claimed (if left blank, then there are none):

Non-Priority Application No.	Country	Filing Date (MM/DD/YYYY)

I hereby claim the benefit under 35 U.S.C. §119(c) of any United States provisional applications listed below:

Application No.	Filing Date (MM/DD/YYYY)

I hereby claim the benefit under 35 U.S.C. §120 of any prior U.S. non-provisional application(s) or under §365(c) of any prior PCT international application(s) designating the U.S., listed below and, insofar as the subject matter of each of the claims of this application is not disclosed in such U.S. or PCT international application in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose to the PTO all information which is material to patentability as defined in 37 C.F.R. §1.56 which became available between the filing date of the prior application and the national or PCT international filing date of this application:

Application No.	Filing Date (MM/DD/YYYY)	Status (patented, pending, abandoned)

As a named inventor, I hereby appoint the following registered practitioners to prosecute this application and to transact all business in the Patent and Trademark Office connected therewith:

All of the practitioners associated with Customer Number 001444

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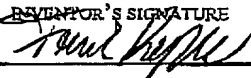
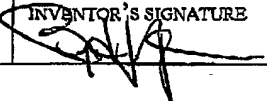
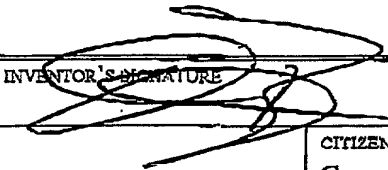


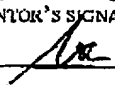
Title ZINC SULPHIDE ELECTROLUMINOPHORES AND METHOD FOR PRODUCTION THEREOF

U.S. Application filed _____, Serial No. _____

PCT Application filed _____, Serial No. _____

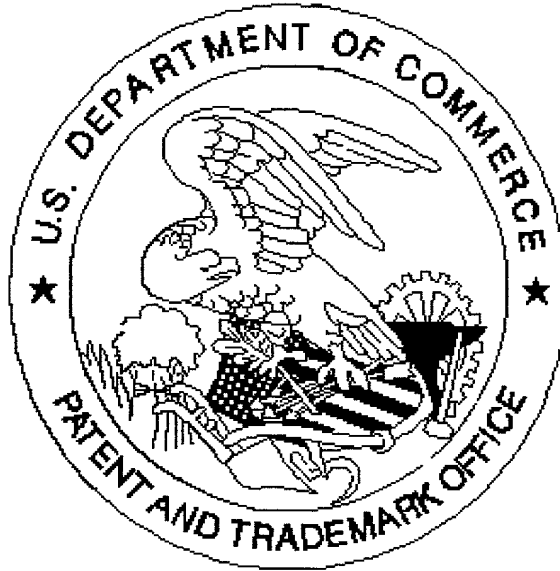
The undersigned hereby authorizes the U.S. Attorneys or Agents appointed herein to accept and follow instructions from Dr.-Ing. Peter Riebling as to any action to be taken in the U.S. Patent and Trademark Office regarding this application without direct communication between the U.S. Attorneys or Agents and the undersigned. In the event of a change of the persons from whom instructions may be taken, the U.S. Attorneys or Agents appointed herein will be so notified by the undersigned.

I hereby further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under 18 U.S.C. §1001 and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

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